

Synthesis and Electrochemical Properties of Non-stoichiometric $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$

Yun Yang, Hua Li, Chuanqi Feng*, Xiao Chen, Shengfu Wang

College of chemistry and chemical engineering, Hubei University, Wuhan 430062, P.R.China

86981079@qq.com; *cfeng@hubu.edu.cn

Abstract

$\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ was synthesized by rheological phase reaction method. The XRD technology was used to analyze the structure of samples. The method of transmission electron microscope was taken to observe morphology of the particles. The electrochemical properties were also studied. The results show that the non-stoichiometric $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ as a cathode material behaves excellent electrochemical properties to compare with pure LiFePO_4 . The initial discharge capacity of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ arrived at 154 mAh/g at 0.1 C. The discharge capacity of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ was retained at 139 mAh/g after 100 cycles. The $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ still behaved better performances at higher charge/discharge rate (1C). The possible reasons for $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ to behave outstanding electrochemical properties are discussed also.

Keywords

Lithium Ion Battery; Inorganic Synthesis; Electrochemical Properties; LiFePO_4

Introduction

With the development of technology, many portable electronic devices have been applicable in our daily life. Meanwhile, the batteries of the devices have been required for better electrochemical performances. During these years, more researchers have founded that, some crucial factors influence the electrochemical properties, such as the cathode materials, anode materials, the electrolytes and the separators, especially the cathode and the anode materials are the most important factors. The choice of the cathode materials is focused on layered compounds Li_xMO_2 and spinel compounds $\text{Li}_x\text{Mn}_2\text{O}_4$ ($\text{M}=\text{Co}, \text{Ni}, \text{Mn}, \text{V}$ etc.). The layered LiCoO_2 , which holds stable properties and is easy to be synthesized, has already achieved a large-scale industrial production. However, LiCoO_2 is toxic compound and needs handing and disposal carefully, so people try to replace LiCoO_2 for lithium ion batteries with other compounds, like LiNiO_2 , LiMnO_2 , LiMn_2O_4 , LiFePO_4 and so on.

Since 1997, the electrochemical properties of LiFePO_4

was first introduced by Goodenough and co-workers, due to its incomparable advantages, such as low-cost and free from environmental pollution. As the LiFePO_4 has a high theoretical capacity of 170 mAh/g and a very flat discharge platform at 3.4 V *Versus* Li/Li^+ , the good cycle stability, and the excellent thermal stability, it becomes a hot research project. In spite of these attractive features, LiFePO_4 cathode material has two defects, such as the low ionic and electronic conductivity, which has greatly inhibited its actual applications. So people started to improve properties of LiFePO_4 by two ways, one is coating of LiFePO_4 with electrically conductive materials like carbon, metal and metal oxides, the other is to control the particle size by coating with carbon and doping with metal ions. Carbon coating is a common method, because it can effectively improve the conductivity of the LiFePO_4 . But there is a loss of energy density by the inaction with the carbon, also it can't help with the chemical diffusion coefficient of lithium in the crystal. Heaven never seals off all the exits. Recently, some reported that, doping with metal can effectively improve the performance cycle. For example, some people try to dope with Mg, Ti, Zr, Cr, Nb and Mo to replace a little number of Li, so it can feasibly enhance the intrinsic conductivity. Other people attempt to dope in Fe-site with V, Ni, Co, Mg, and Zn, which can improve the electrochemical performance of LiFePO_4 by increasing the intrinsic electronic conductivity of LiFePO_4 . Our research work in this paper focuses on synthesis and its electrochemical performances of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$.

Experimental

Stoichiometric amounts of $\text{LiAc}\cdot 2\text{H}_2\text{O}$, $\text{FePO}_4\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{W}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$ and polyethylene glycol (PEG; mean molecular weight of 3400, 250 g PEG/mol FePO_4) powders were used as the starting materials through rheological phase reaction method, the molar of $\text{Li}: \text{Fe}: \text{W}=1:1:0.01$. They were mixed by grinding for

10min, and then an appropriate amount of water was added to get a rheological state. It was dried to form precursor at 110°C for 10 hours. Finally, the resulting precursor was heated in a tube furnace to get the powders of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ at 700°C for 12h in Argon atmosphere.

X-ray diffraction (XRD) tests of the samples were carried out on a shimadzu XRD-6000 diffractometer using Cu K α radiation. The morphology and size of powders were observed by TEM on a JEM21002CX2 II using the accelerated voltage (80 kV).

The electrochemical performances were examined by a Shenzhen Neware battery program-controlled test system. The products were mixed with 20 % (weight) carbon black and 5 % (weight) PVDF. The mixture was rolled into a film and was dried at 125°C for 24 h in vacuum. The film was then cut to size (1 cm²) and pressed onto a nickel mesh (1 cm²). Coin test cells were assembled in an argon-filled glove box, with a metallic Li counter electrode, Celgard 2400 microporous membrane separator, and 1 M LiClO₄ electrolyte dissolved in a 50/50 vol% mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The cells were charged and discharged between 2.5 and 4.2 V at room temperature. In the electrochemical impedance spectroscopy (EIS) measurements, the cells were tested in a Shanghai electrochemistry station.

Results and Discussion

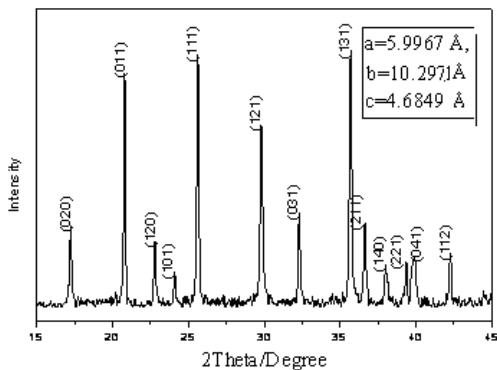


FIG. 1 XRD PATTERNS OF $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$

The XRD patterns of the $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ powders show in Fig.1. XRD showed that the sample was single-phase olivine-type structure. The XRD patterns of the sample are agreement well with that of phospho-olivine LiFePO_4 indexed with orthorhombic Pnma space group(40-1499),and no other impurity

phase was detected. The sample has narrow diffraction peaks, which indicates a good crystallinity. The cell parameters of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ calculated by the XRD are that $a=5.9967 \text{ \AA}$, $b=10.2971 \text{ \AA}$ and $c=4.6849$. Compared with cell parameters of pure LiFePO_4 ($a=6.019, b=10.347$ and $c=4.704$), the a , b , c of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ are decreased. It showed that tungsten dopant has been successfully doped into LiFePO_4 without affecting the phospho-olivine structure. The W⁶⁺ may be doped into M1(Li site) or M2 sites (Fe site). When W⁶⁺ is occupied on the Li site (M1), it will lead Li vacancies on M1 to compensate. When W⁶⁺ is occupied on the Fe site (M2), the Fe²⁺ will be driven to the Li site (M1). The radio of Li⁺ and Fe²⁺ is 0.068 and 0.074 nm separately. According to the rule that the ions with close radio are easy to be substituted, it was deduced that W⁶⁺ was preferred to occupy the Li site (M1). Low concentration tungsten doping leads to the shrinkage of crystal cell due to that the radius of W⁶⁺ ion (0.062 nm) is smaller than that of Li⁺ ion(0.068 nm).

In Fig.2, It was observed that the particles of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ sample take on a spherical shape, the dark grey region is the particle and the light grey region is the carbon coating on the particles. The thickness of the coating amounts to several nanometers, which suggests that carbon would have played a role in forming a network structure, thereby reducing the particle size. The particle size was found to be between 0.5 and 1 μm . On the basis of conductivities measurements, it can be concluded that tungsten doping has effect on the improvement of electronic conductivity.

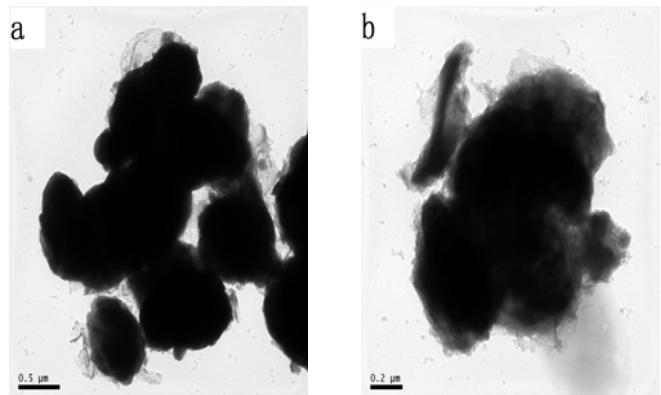


FIG. 2 TRANSMISSION ELECTRON MICROGRAPH OF $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$

The initial charge/discharge curves and cycle life discharge curves of LiFePO_4 (A) and $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ (B) at 0.1 C are shown in Fig.3 and Fig.4. The Fig.3 showed that $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ (B) has higher capacity than that of LiFePO_4 . The charge and discharge capacities of the

$\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ are 162, 154 mAh/g (at 0.1 C rate) respectively, while charge and discharge capacities of LiFePO_4 are 138 and 121 mAh/g. The specific charge capacity of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ is near to theoretical capacity of LiFePO_4 . From Fig.4 it can be seen that at the rate of 0.1 C, the sample of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ has the specific discharge capacity of 154 mAh/g, after 100 cycles, the specific discharge capacities remained at 139 mAh/g, but the specific discharge capacity of LiFePO_4 remained only 114 mAh/g, which is lower than that of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ after the same cycles. LiFePO_4 doped with W^{6+} has greatly improved conductivity and promotes Li^+ diffusion, both of which lead to a lower loss of capacity during cycling.

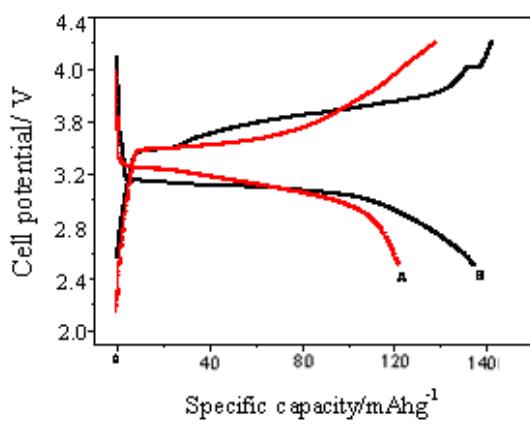


FIG. 3 THE INITIAL CHARGE/DISCHARGE CURVES OF LiFePO_4 (A) AND $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ (B) AT 0.1 C

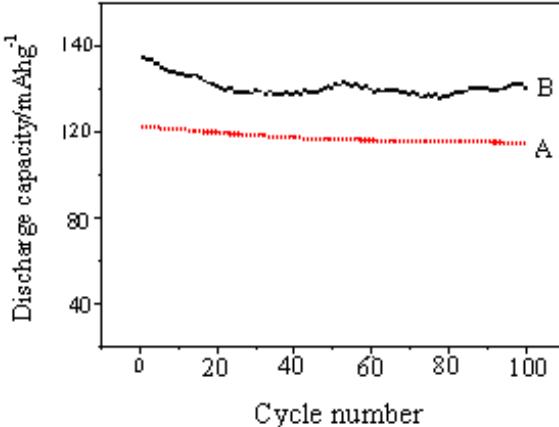


FIG. 4 CYCLE LIFE DISCHARGE CURVES OF LiFePO_4 (A) AND $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ (B) AT 0.1 C

Fig.5 shows the initial charge/discharge curves of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ at various C-rates. At the rates of 0.2 and 0.5 C, the initial specific charge-discharge capacities are 151, 150 mAh/g and 137,136 mAh/g respectively, while at the high rates of 1C, the initial

specific charge-discharge capacities are 122,124 mAh/g respectively. It indicates that the specific capacity was strongly affected by the discharge current, especially in the high current range.

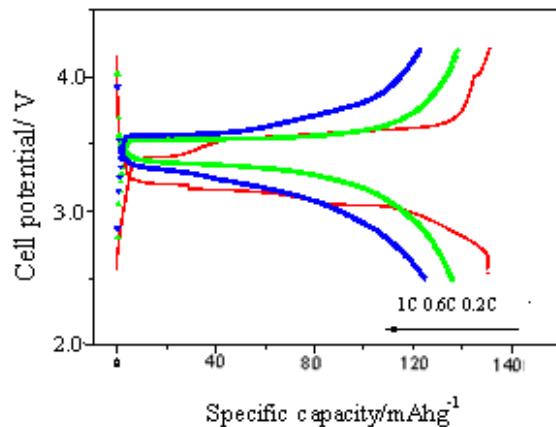


FIG. 5 THE INITIAL CHARGE/DISCHARGE CURVES OF $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ AT VARIOUS C-RATES (0.2,0.6 AND 1 C)

Fig.6 shows the cycling behaviors of the $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ at room temperature. At the rates of 0.2, 0.5 and 1 C, the sample has the specific discharge capacities of 150, 136,124 mAh/g, after 100 cycles, as well as the specific discharge capacities remained 130, 120 and 109 mAh/g respectively.

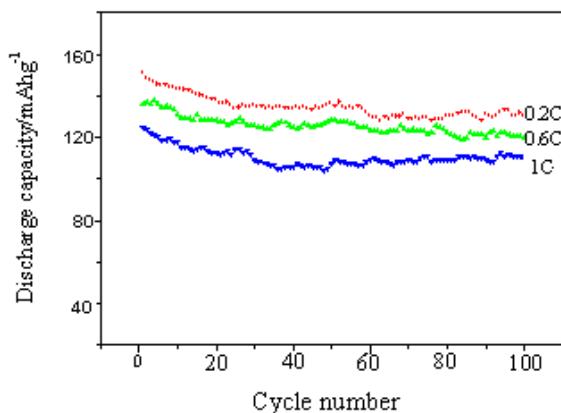


FIG. 6 CYCLE LIFE DISCHARGE CURVES OF $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ AT VARIOUS C-RATES (0.2,0.6 AND 1 C)

The good cycling behaviors of the sample are mainly attributed to the enhancement of the electronic conductivity by doping with W^{6+} . The polarization of the electrodes due to electronic conductivity becomes an influential factor, which determines the kinetics of the electrochemical reaction of the electrodes when the electrodes are charged and discharged at high rate.

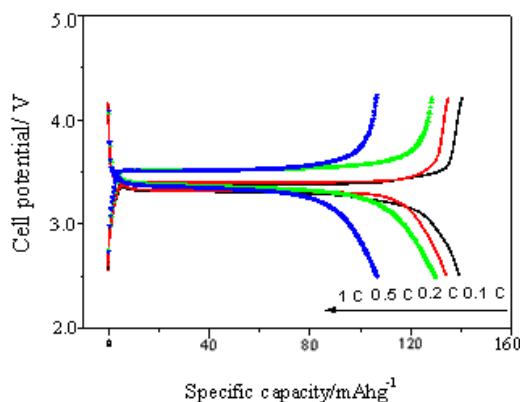


FIG. 7 THE 50TH CYCLE OF $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ AT VARIOUS C-RATES (0.1, 0.2, 0.5 AND 1 C)

Fig.7 show the 50th cycle of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ at various C-rates. On the curve, we can see that in the case of 0.1 C and 0.2 C, the charge-discharge curves have similar flat plateaus, the charge voltage plateau is 3.36 V, while the discharge voltage plateau is 3.30 V, the potential intervals is 0.06 V. The sample shows a smaller value of potential interval compared with that reported in references, which indicates the enhancement of electrode reaction reversibility. In the case of 0.5 C and 1 C, the charge-discharge curves have similar flat plateaus, the charge voltage plateau is 3.42 V, while the discharge voltage plateau is 3.30V. At various C-rates, the $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ electrodes exhibited very flat charge and discharge plateaus, which implies that the two-phase redox reaction proceeds between LiFePO_4 and FePO_4 . Long flat voltage-plateau appears to indicate higher specific charge-discharge capacity.

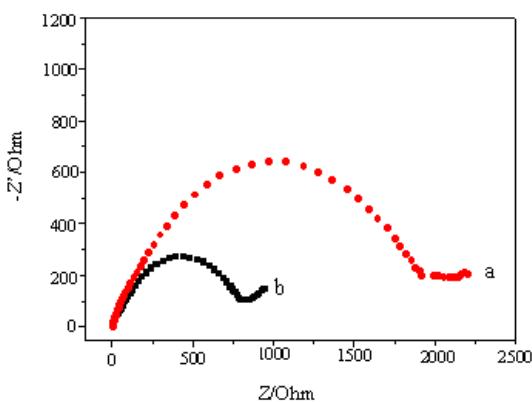


FIG. 8 TYPICAL ELECTROCHEMICAL IMPEDANCE SPECTRA OF (A) LiFePO_4 AND (B) $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ ELECTRODE IN THE FREQUENCY RANGE BETWEEN 100KHZ AND 10 MHz

Fig.8 shows the typical electrochemical impedance spectra of LiFePO_4 and $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ electrode, which

was measured before electrochemical properties testing. It can be seen that the plots are composed of two parts, the depressed semicircles in high-frequency range and the lines in low-frequency range. The resistance of the semicircles is related to the complex reaction process of electric charge transfer. The resistance of the lines showed a typical Warburg behavior which is attributed to the diffusion of lithium ion in the bulk of the cathode materials. The numerical value of the diameter of the semicircle on the Z_{re} axis is equal to the charge transfer resistance (R_{ct}) or the so-called the interfacial resistance. Comparing the semicircles of the LiFePO_4 and $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ samples in the moderate frequency region, it is evident that the R_{ct} of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ has been decreased. When LiFePO_4 was doping with W, it is more favorable for lithium ions migration, and therefore the electrochemical performances were improved.

Conclusions

The $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ has been successfully synthesized through rheological phase reaction using PEG as a reductive agent. The XRD data can prove that $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ has the same structure as that of LiFePO_4 . The size of particles is distributed from 0.5 μm to 1 μm . The specific discharge capacity of $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ at 0.1 C was 154 mAh/ g. After 100 cycles, the discharge capacity still retained at 139 mAh/ g. Compared with the pure LiFePO_4 , the $\text{Li}_{1-x}\text{W}_{0.01}\text{FePO}_4$ behaved excellent electrochemical performances. So it can be a promising cathode material for lithium ion battery application.

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Chuanqi Feng was born on 23, Feb. of 1957 in Xianning city, Hubei province, P.R China. He got Ph.D in 2003 at Wuhan University, P.R China. He is working for college of chemistry and chemical engineering, Hubei University as a Professor. The major field of study is lithium ion battery materials.